Sodium Compounds in Portland Cement.

A BULLETIN of the United States Bureau of Standards (Research Paper No. 414), entitled "System CaO-Na$_2$O-Al$_2$O$_3$," gives the results of a continuation of studies begun several years ago by Messrs. L. T. Brownmiller and R. H. Boyne, to determine the constitution of Portland cement clinker and the part played by each of the compounds in the manufacture and use of the product. A part of the system CaO-Na$_2$O-Al$_2$O$_3$, in the region low in Na$_2$O, has been investigated by the methods of phase equilibria. The stability fields, boundary curves, and invariant points have been defined. Optical and X-ray data are presented and ternary diagrams introduced to indicate the composition and temperature relations and the course of crystallization in the system.

To-day the studies are fairly complete for the principal constituents of Portland cement, namely, for CaO, SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, and MgO; and from them the modern ideas on the constitution of cement have been evolved. Besides these components, there are many others occurring in small amounts in cements. Of the minor components, soda is one of the more important, since it is common to practically all cements. Therefore a continuation of these studies has been made to determine the combinations which soda is capable of forming with the other constituents of the cement.

The system CaO-Na$_2$O-Al$_2$O$_3$ has now been examined and constitutes the subject of this report. This system, however, was not explored completely. Not only would special methods have to be adopted to solve it entirely, but, in cements, the concentration of soda is small; hence, the studies in the system could be confined to compositions low in Na$_2$O. Apparently only one compound of CaO and Al$_2$O$_3$, 3CaO.Al$_2$O$_3$, occurs in normal Portland cements; accordingly, that region of the diagram CaO-Na$_2$O-Al$_2$O$_3$ in which 3CaO.Al$_2$O$_3$ occurs is the field of greatest importance. Nevertheless, because of the complexity of the system, other portions of the diagram had to be investigated to understand fully the relations in that region.

Because of the volatility of Na$_2$O at temperatures above 900 deg. C., special methods had to be used in preparing the samples. Base compositions of CaO and Al$_2$O$_3$ were weighed in various proportions, thoroughly mixed by stirring in a small amount of water, and then burned in a platinum resistance furnace. A portion of about 5 g. of this base composition was weighed and to it the third component, Na$_2$O, was added in the form of Na$_2$CO$_3$. An excess of the sodium carbonate over that desired in the final sample was required since some Na$_2$O is volatilized on heating. After dry mixing the components of the ternary com-

position, it was burned at a temperature of about 1,400 deg. C., pulverized, and reburned at a higher temperature. Burning was done in an open platinum boat in a platinum-resistance furnace. After cooling in a desiccator, the sample was weighed, and from the difference in weight the amount of Na_2O remaining in the mixture was calculated. Relatively low temperatures were used for the first burning because this procedure resulted in less loss of Na_2O by volatilization than was obtained with high initial burning temperatures. The amount of Na_2O lost on subsequent heatings at 1,400 deg. C. to 1,500 deg. C. was found to vary from less than 1 per cent. of the total weight in samples low in soda to somewhat larger percentages in samples high in soda. In making up the compositions for these studies, an excess of about 25 per cent. of sodium carbonate above the theoretical amount required was weighed into the base compositions, but this percentage excess could be reduced somewhat if the first burning were made at temperatures as low as about 1,100 deg. C. On twice burning such a mixture at 1,400 deg. C. to 1,500 deg. C. the composition was found usually to be within 1 per cent. of that desired. Further adjustments could then be made to give the precise compositions required. The second heating of the samples was necessary before final weighing because frequently not all of the carbon dioxide was evolved during the first burning, as evidenced by effervescence on treating with hydrochloric acid. Before final weighing, all samples were heated at least once to temperatures of about 1,500 deg. C.

That portion of the CaO-Na_2O-Al_2O_3 system in the neighbourhood of $3CaO.Al_2O_3$ and low in soda is the region directly concerned with Portland cement. From this work alone, however, the authors state they cannot predict the combinations of soda in cement; to do so a study must be made of systems involving the other components of cements with soda. However, it is clear that of the compounds of CaO, Na_2O, and Al_2O_3 which are important in solving the final status of the Na_2O in cement, $8CaO.Na_2O.3Al_2O_3$ alone is of significance. This is due to the existence in Portland cement of $3CaO.Al_2O_3$ alone, of the compounds of lime and alumina, and the finding in this study that the field of $3CaO.Al_2O_3$ adjoins that of $8CaO.Na_2O.3Al_2O_3$, but not that of $3CaO.2Na_2O.5Al_2O_3$. The stability of $8CaO.Na_2O.3Al_2O_3$ with the other constituents of cement, $3CaO.SiO_2$, $2CaO.SiO_2$, $4CaO.Al_2O_3.Fe_2O_3$, and MgO, must therefore be determined before the composition of the compounds of soda in cements can be defined.

Any direct attempt to identify $8CaO.Na_2O.3Al_2O_3$ in a commercial or laboratory cement probably would be unsuccessful. Identification by the microscope would be extremely difficult, since the compound must necessarily be present only in small amounts and the similarity of optical properties of $8CaO.Na_2O.3Al_2O_3$ and the other cement compounds makes difficult its differentiation from them by microscopic means. Likewise, the X-ray method cannot be used to advantage because the principal lines of the diffraction pattern of $8CaO.Na_2O.3Al_2O_3$ coincide with those of $3CaO.Al_2O_3$, and only if $8CaO.Na_2O.3Al_2O_3$ were present in excessive amounts could we hope to establish its presence in cements. Hence thermal studies alone furnish the basis for establishing the nature of the soda compounds in cement. If thermal studies show that $8CaO.Na_2O.3Al_2O_3$ is stable in the presence of $3CaO.SiO_2$, $2CaO.SiO_2$, $4CaO.Al_2O_3.Fe_2O_3$, and MgO, we are assured that Na_2O may exist in cement in the form of that ternary compound. In that case the Na_2O may replace some of the CaO from $3CaO.Al_2O_3$ and form the new combination $8CaO.Na_2O.3Al_2O_3$. Former studies in this laboratory have indicated that Na_2O replaces CaO when the former is added to cement compositions, but this does not necessarily mean that the replacement must be in $3CaO.Al_2O_3$. It might be a replacement in $4CaO.Al_2O_3Fe_2O_3$ or the silicates. These questions can be solved only by further study of the soda systems with the other components of cement.

The Thermochemistry of Cement Burning.

By R. ZOLLINGER.

THIS article is based on the formula for an ideal cement developed by the author in a former paper, viz. $x(3CaO.SiO_2)y(3CaO.R_2O_3)$. Assuming it to be composed of ideal raw materials, viz. the purest kaolin and limestone, this cement molecule is expressed quantitatively by the formula $9.CaO.2SiO_2.1.Al_2O_3$, or $2(3CaO.SiO_2).1.(3CaO.Al_2O_3)$.

It will be assumed that the reaction of cement formation commences at 1,500 deg. C., and that the specific heats of the various materials involved are : CaO 0.1882, SiO_2 0.1887, and Al_2O_3 0.2003.

The following amount of heat will thus be required to raise the cement molecule to 1,500 deg. C.

$$0.1882 \times 9 \times 56.08 \times 1,500 = 142,470 \text{ kcal.}$$
$$0.1887 \times 2 \times 60.3 \times 1,500 = 34,215 \text{ ,,}$$
$$0.2003 \times 102.2 \times 1,500 = 30,705 \text{ ,,}$$

Total   207,390   ,,

This heat is held by the cement clinker by virtue of its specific heat, and is conveyed by the clinker to the cooler. It is abstracted from the clinker by the secondary air passing through the cooler and is thus in the main returned to take part in the burning process. The only portion that is lost is the small amount corresponding to the temperature of the clinker on leaving the cooler. This loss depends upon the efficiency of the cooler, and assuming the clinker leaves at 50 deg. C.—a temperature which must be attained with a good cooler —the loss is

$$727.52 \times 50 \times 0.152 = 5,529 \text{ kcal.}$$

727.52 being the weight per kg.-molecule of the cement and 0.152 the specific heat of the clinker calculated from the above data. In practice the loss will be somewhat higher than this, since a certain amount of additional heat is held by the coal ash contained in the clinker. The value 6,000 kcal. may therefore be conveniently taken as the heat lost in the clinker.

From the formula $9CaO.2SiO_2.Al_2O_3$ the weight of a kg.-mol. of cement is 727.52 kg., which corresponds to 1123.52 kg. raw meal, since the 9 molecules of CaO are combined with 9 molecules of CO_2. If 425 kcal. are required to calcine 1 kg. of $CaCO_3$, the heat required to calcine 9 molecules of $CaCO_3$ is $9 \times 100.08 \times 425 = 391,730$ kcal.

The actual reaction of cement formation, once the reaction temperature is reached, proceeds exothermically. It thus contributes to the process a quantity of heat of which the exact magnitude has not been established. In practice the value 20,000 kcal. per 1,000 kg. clinker may be taken, which reduces the heat required from the fuel by about 15,000 kcal. per kg.-mol. of cement.

There are, however, further heat-consuming factors involved. First there is the evaporation and superheating to the temperature of the exit gases of a quantity of water depending on the nature of the process ; further there is the necessity of heating the CO_2 evolved on calcination to the exit gas temperature ; while finally the combustion gases reach the stack at the high exit temperature. Steam, CO_2 and combustion gases together form the entire gases of the process, and their heat content on entering the stack gives the total waste gas loss.

The final loss factor is the radiation from the kiln, etc. This may be taken under normal conditions as 50,000 kcal. for a wet-process kiln and 60,000 kcal. for the dry process. The dry-process figure is higher for the same conditions —i.e., for the same exit-gas temperature in the two processes—because the dry-

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process kiln must be considerably longer and thus has a greater radiating surface.

On the basis of these generally valid numerical data, the heat balances for certain examples will be more closely considered. In each instance the calculations refer to a daily output of 150 tons, a figure which may be accepted as normal. Both wet and dry processes are studied, each being subdivided into the two cases in which the waste gases have final temperatures of 300 deg. C. and 100 deg. C. respectively.

There are thus the following four cases :

(1) The dry-process with 10 per cent. water in the raw meal, the exit-gas temperature not exceeding 300 deg. C.

(2) The dry process with 10 per cent. water in the raw meal, the exit-gas temperature not exceeding 100 deg. C.

(3) The wet process with 36 per cent. water in the raw meal, the exit-gas temperature not exceeding 300 deg. C.

(4) The wet process with 36 per cent. water in the raw meal, the exit-gas temperature not exceeding 100 deg. C.

It will be assumed that the same coal is used in all cases, its percentage analysis being : carbon 80, hydrogen 5, oxygen plus nitrogen 8, sulphur 2, calorific value 7,500 kcal. per kg. (13,500 B.T.U. per lb.). The air requirement of this coal may be calculated as follows :

$$\text{Air} = (2.667C + 8H + H + S)\,\frac{100}{21}$$

$$= 2.62 \times \frac{100}{21} \times 1.2 \times 0.7 = 10.48 \text{ cu. metres per kg. coal.}$$

The figure 1.2 is the excess air factor for normal working. The combustion gases occupy the same volume as the air for combustion at the same temperature. Calculating to the exit temperature we find the heat lost in the combustion gases to be

$$10.48\left(1 + \frac{T}{273}\right) \times \text{sp. ht.} \times (T - 273),$$

where T is the absolute temperature. Thus in cases (1) and (3) the heat lost in the exit gases per 1 kg. coal is

$$10.48 \times \frac{573}{273} \times 0.33 \times 300 = 2,119 \text{ kcal.}$$

For cases (2) and (4) it is

$$10.48 \times \frac{373}{273} \times 0.33 \times 100 = 475 \text{ kcal.}$$

Thus the quantities of heat available for cement burning, per kg. of coal used (i.e., per 7,500 kcal. of heat generated), are 5,301 kcal. for cases (1) and (3) and 7,022 kcal. for cases 2 and 4.

Heat is required for evaporating the water and superheating it to the exit-ga temperature. For the evaporation 595 kcal. per kg. of water are required. The superheat factor for superheating to 300 deg. C. is 140 kcal., and for 100 deg. C. it is 46 kcal. Thus the total heat requirement for evaporation and superheating per kg.-mol. cement is

Case (1) 112.35 (595 + 140) = 82,504 kcal.
  ,, (2) 112.35 (595 + 46)   = 71,952 ,,
  ,, (3) 404.47 (595 + 140) = 297,285 ,,
  ,, (4) 404.47 (595 + 46)   = 258,265 ,,

The CO_2 from the raw materials must be raised to either 100 or 300 deg. C. Assuming a specific heat of 0.225 for 100 deg. C. and 0.209 for 300 deg. C., the heat required for this amounts to

Cases (1) and (3) 24,829 kcal. per kg.-mol. cement.
  ,, (2) and (4) 8,910 ,,   ,,   ,,   ,,

The coal consumption can now be calculated as follows :

CASE (1).—391,730 kcal. for calcination.
    6,000   ,,   ,, heat lost in clinker.
   60,000   ,,   ,, radiation loss.
   82,504   ,,   ,, water evaporation and superheating.
   24,829   ,,   ,, heating CO_2.

  565,063   ,, per kg.-mol. cement.

$$= \frac{565,063}{5,301} = 106.5 \text{ kg. coal} = 14.30 \text{ per cent.}$$

The actual heat supplied is $106.5 \times 7,500 + 15,000$ (from exothermic reaction) $= 813,750$ kcal.

CASE (2).—391,730 kcal. for calcination.
    6,000   ,,   ,, heat lost in clinker.
   60,000   ,,   ,, radiation loss.
   71,952   ,,   ,, water evaporation and superheating.
    8,910   ,,   ,, heating CO_2.

  538,592   ,, per kg.-mol. cement.

$$= \frac{538,592}{7,022} = 77.2 \text{ kg. coal} = 10.65 \text{ per cent.}$$

The actual heat supplied is $77.2 \times 7,500 + 15,000$ (exothermic) $= 594,000$ kcal.

CASE (3).—391,730 kcal. for calcination.
    6,000   ,,   ,, heat lost in clinker.
   50,000   ,,   ,, radiation loss.
  297,285   ,,   ,, water evaporation and superheating.
   24,829   ,,   ,, heating CO_2.

  769,844   ,, per kg.-mol. cement.

$$= \frac{769,844}{5,301} = 145.0 \text{ kg. coal} = 19.90 \text{ per cent.}$$

The actual heat supplied is $145.0 \times 7,500 + 15,000$ (exothermic) $= 1,102,000$ kcal.

CASE (4).—391,730 kcal. for calcination.
    6,000   ,,   ,, heat lost in clinker.
   50,000   ,,   ,, radiation loss.
  258,265   ,,   ,, water evaporation and superheating.
    8,910   ,,   ,, heating CO_2.

  714,905   ,, per kg.-mol. cement.

$$= \frac{714,905}{7,022} = 103.0 \text{ kg. coal} = 13.90 \text{ per cent.}$$

The actual heat supplied is $103.0 \times 7,500 + 15,000$ (exothermic) $= 787,500$ kcal.

If the heat of the clinker were not recovered it would in all cases be necessary to add to these figures the 207,390 kcal. necessary to initiate the clinkering reaction, less the 6,000 kcal. entered as lost in the clinker.

Comparison of the foregoing cases shows the superior heat economy of the dry process for equal exit-gas temperatures. In this connection it must not be forgotten, however, that the attainment of equal exit-gas temperatures necessitates a much longer kiln in the dry process.

The greatest possibility of reducing heat consumption lies in reducing the exit gas temperature. In practice this is limited by the necessity for maintaining a chimney draught corresponding to working conditions. The draught depends on the height of the stack and its relation to the exit-gas temperature.

Lower temperatures require a considerably higher stack to give the same draught. It is only rarely that stacks more than 200 ft. in height are built, and stacks of this height require an exit-gas temperature of about 300 deg. C. If it is desired to attain lower temperatures, i.e., lower heat consumption and fuel economy, it is better to utilise the waste gases outside the kiln for drying or raising power. The following calculations show the relationship between exit-gas temperature and height of stack.
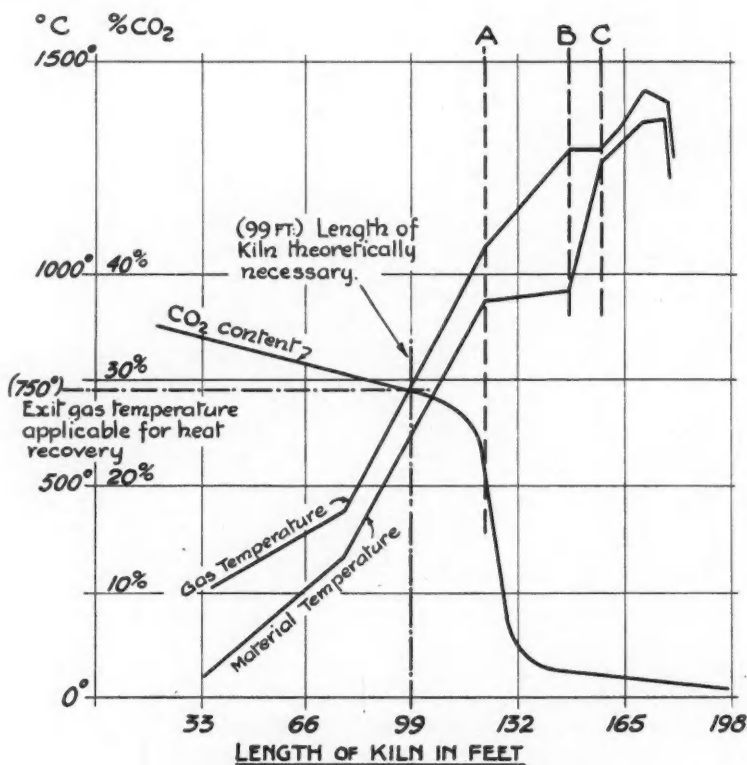

Fig. 1.—Heat Reactions in the Rotary Kiln.

The normal draught at the base of the stack may be taken to be $z = 30$ mm. water gauge. The stack height is given by the formula

$$h = \frac{z}{273 \left(\dfrac{1.293}{273 + t_{air}} - \dfrac{1.35}{273 + t_{exit\ gases}} \right)}$$

From this formula the height of stack for cases (1)–(4) is: (1) and (3), 300 deg., height = 170 ft. ; (2) and (4), 100 deg., height = 410 ft.

The cross-sectional area of the stack is a function of the volume and velocity of the exit gases :

$$\text{Area} = \frac{\text{Gas volume per second}}{\text{Velocity}}$$

$$\text{Volume per second} = \frac{\text{Volume per kg.-mol.} \times 150{,}000}{84{,}000 \times 727.52} \text{ cubic metres.}$$

on the assumption of 150 tons (150,000 kg.) daily output.   The cross-sectional area of the stack for cases (1) to (4), assuming the same velocity of 25 metres per second, is as follows :

CASE (1) : Exit gas per kg.-mol. cement = 3062.4 cubic metres = 76.56 cu. metres per second.   Cross-section = 76.56/25 = 3.06 sq. metres (33 sq. ft.).

CASE (2) : Exit gas per kg.-mol. cement = 1564.6 cu. metres = 39.10 cu. metres per second.   Cross-section = 39.10/25 = 1.58 sq. metres (17 sq. ft.).

CASE (3) : Exit gas per kg.-mol. cement = 4672.6 cu. metres = 116.81 cu. metres per second.   Cross-section = 116.81/25 = 4.67 sq. metres (50 sq. ft.).

CASE (4) : Exit gas per kg.-mol. cement = 2425.9 cu. metres = 60.65 cu. metres per second.   Cross-section = 60.65/25 = 2.42 sq. metres (26 sq. ft.).

It will be interesting to apply the four cases discussed to the construction of the rotary kiln, but certain general questions must first be dealt with.   Since fuel and raw material travel in opposite directions in the rotary kiln, the heat exchange is very efficient and there is a continuous fall in temperature along the kiln, the nature of which is illustrated by Nacken's well-known curves in Fig. 1.   The combustion gases give up their heat to the raw materials, the temperature of which rises as the gas temperature falls.   By including the CO_2 curve in the diagram the conditions in the kiln become readily understood. From the head of the kiln to point A we are dealing with pure heat exchange. Between A and B calcination rapidly proceeds, and the heat consumed is much greater.   In this zone the temperature of the raw materials remains almost constant in spite of continuous absorption of heat.   Between B and C the temperature of the kiln gases remains constant.   Since the temperature of the raw materials is raised in this zone, we must conclude that heat is given to the gases by the raw materials.   In this zone the true process of cement formation takes place, and this is known to be exothermic.   The accuracy of Nacken's curves cannot be disputed since they have been checked and confirmed repeatedly. Although they were obtained by experiment on a rotary kiln 197 ft. long and 10 ft. diameter, they naturally apply, suitably extended or contracted, to all other kilns, including even the shaft kiln.

The ideal heat exchange is naturally attained when the cross-section of the kiln is completely utilised, as in the shaft kiln.   In the rotary kiln only 7 to 15 per cent. of the cross-section is utilised, and to attain an economical heat exchange in spite of this the kiln must be correspondingly lengthened.   The length depends upon the exit-gas temperature it is desired to obtain.   If the dry and wet processes are compared it is obvious that much more water needs to be evaporated in the wet process, and that as a result of this and of the increased fuel consumption necessary to evaporate the water larger volumes of gas are present.   Since the heat exchange depends on the gas speed, and the speed upon the kiln cross-section, it follows that the wet-process rotary kiln must have a greater cross-section than the dry-process kiln.   On the other hand the increased quantity of gas absorbs correspondingly more heat, so that the Nacken curves for the wet process will fall more steeply as the kiln head is approached.   In other words, a shorter wet-process kiln is required if the exit gas temperatures in the two processes are to be equal.

The various relationships may be summarised as follows.   The exit-gas temperature, which is of the first importance to the heat economy of the process, depends on the height and cross-section of the chimney, which are factors of the

draught and kiln length.   The longer the kiln the lower the exit-gas temperature, but, on the other hand, the greater the initial cost of the plant.

With the same output and exit-gas temperature a shorter kiln of greater cross-section is required for the wet process than for the dry.

The gas velocity depends on the kiln cross-section.   On the other hand a change in the cross-section means that a different proportion of it is occupied by the cement materials, assuming the output to be the same.   With a smaller cross-section a larger part of the cross-sectional area is utilised than in the case of a kiln of greater section.   In order to attain the same conditions of burning in spite of this, the kiln speed must be varied, i.e., a kiln of small section must rotate more slowly than a wider kiln.   The rotation of the kiln causes the cement material to roll round and down the kiln, so that if the speed of rotation were the same for kilns of different sections the distance travelled by the material in a narrower kiln would be less than with a wider cylinder, and a shorter time would be spent in the kiln.   The heat exchange would thus be less satisfactory in the narrower kiln.

Thus from the purely technical point of view extensive calculations are necessary to decide between the wet and the dry processes.   Again the attainment of a low exit-gas temperature is by no means so simple a question as it may appear. Under certain circumstances it may be necessary to avoid the use of long kilns and costly stacks, and to withdraw the exit gases from the kiln at a high temperature and to use them outside the kiln for drying or generating power.   The height of the stack may be assisted to a great extent by using forced draught, although in practice there is a definite limit to this.

There is no doubt, in general, that it is more correct to use the waste gases so far as possible in the burning process rather than couple the latter with other processes such as drying and power production.   The method to be adopted in any particular instance depends on the local conditions, and is a matter for calculation.   If it is decided to recover the heat from the gases outside the rotary kiln it is naturally most profitable to keep the kiln as short as possible, i.e., to keep the exit gas temperature as high as possible.   The Nacken curves show that temperatures below 750 deg. C. are of no importance in the burning process, so that the gases should be removed from the kiln with a temperature of at least 500 deg. C. in order to ensure profitable heat recovery outside the kiln.

Exit gas temperatures of 500 deg. C. can only be attained practically in the dry process, and waste-heat recovery outside the kiln is accordingly only applied in this process.   The best solution of the wet process problem is the adoption of long kilns with low exit-gas temperatures.

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The Norwegian Cement Industry.

H.M. Commercial Secretary at Oslo, in a report on the Economic Conditions in Norway, states that the estimated output of cement in Norway in 1931 did not exceed 50 per cent. of the normal production.   The industry was seriously affected by the restriction of the building and other trades.   Prices for home sales remained practically unchanged, but for export they fell heavily owing to keen competition.   Business in foreign markets was also hampered by increased customs duties and other restrictions as well as by monetary complications. Exports declined from 137,118 tons in 1930 to 83,445 tons in 1931.

Portuguese Regulations for Portland Cement to be Used in Salt Waters.

THE Portuguese Government has added to the Portland Cement Specifications of August, 1930, clauses relating to cement for use in works subject to the action of salt waters. All Portland cement, whether of Portuguese or foreign origin, to be used in works subject to the action of sea or sulphate waters must conform to the following requirements :

Chemical Composition.—Portland cement to be used in works subject to the action of sea or sulphate waters should not contain over 2 per cent. of sulphuric anhydride, 3 per cent. magnesia, or 8 per cent. alumina, nor appreciable quantities of sulphides. The hydraulic modulus—the result of dividing the percentage (in weight) of lime by the result of the addition of the percentages (in weight) of silica, alumina, and iron sesqui-oxide (Fe_2O_3)—must be between the limits 1.8 and 2.2.

Tests.—No Portland cement may be used unless it has been previously submitted in an official laboratory to the mechanical and physical tests prescribed in the Specification of August 28, 1930. Before the cement is used a chemical analysis is to be carried out to determine its composition.

Delivery Conditions.—Each contract must specify whether the cement is to be packed in sacks or barrels ; sacks must have a net weight of 50 kilos (110 lb.) and barrels a net weight of 170 kilos (375 lb.).

The selection of sand for concrete subject to the action of sea water must conform to a granulometric analysis according to Féret's classification and to a chemical analysis (to which Abrams's colorimetric test is added) for the detection of organic matter.

The strength of mortars is to be tested by comparison with compressive strengths at seven days in twelve 1 : 3 mortar cubes, six of them prepared with the sand used in the works and the other six with the standard sand used in the official laboratory. The cubes are to be stored in the same conditions as those to which the concrete will be subjected in use. The sand is to be regularly tested during the course of the work. Soft and friable aggregates must not be used. The slump test is recommended to control the water content of the concrete. Cement is to be measured by weight and the aggregates by volume.

Contractors' tests are to be made on cubes of 20 cm. (8in.) sides. During construction nine test cubes are to be made, three to be tested at seven days, three at twenty-eight days, and three at eighty-four days. Twelve additional blocks are to be made every six months, to be tested at one, three, five, and ten years from the date of manufacture. These cubes are to be in the proportions of 660 lb. of cement to 14 cu. ft. of sand, and 28 cu. ft. of coarse aggregate, and should possess a compressive strength of 2,150 lb. per square inch at seven days, 2,550 lb. per square inch at twenty-eight days, and 3,150 lb. per square inch at eighty-four days.

Belgian Cement Production.

For the period, January to June, 1932, the production of Portland cement in Belgium was 733,500 tons, compared with 926,698 tons for the same period last year. Deliveries show a slight increase, from 869,283 tons for the first half of 1931 to 888,500 tons for the corresponding period this year. Exports of C.B.R. for the five months, January to May (except to Holland, France and Germany) declined from 164,487 tons in 1931 to 115,500 tons in 1932.

Heat Economy in the Cement Industry.—V.

By Dr. HANS BUSSMEYER.

Utilisation of Rotary Kiln Waste Gases for Steam and Power Production.

THE dry-process heat balances given in Table XV (CEMENT AND CEMENT MANUFACTURE, April, 1932) show that, even when the value of x (the number of kg. standard coal used per 1,000 kg. clinker) is low, the exit gas temperature t_g is so high that the utilisation of the waste heat merits serious consideration. The steam pressure and degree of superheat are variable, and values can be adopted sufficiently high to give the maximum power from the heat available.

The wet process heat balances of Table XVI (CEMENT AND CEMENT MANUFACTURE, April, 1932) show that waste heat recovery will not be really profitable until $x = 280$ while b (the percentage of water in the raw materials) is low. In the region of smaller values of x and greater values of b the exit gas temperature is so low that only a low steam pressure and slight superheat are possible. This would necessitate a very great evaporating surface in the boiler, and a prime mover with high steam consumption, so that the heavy cost of the initial plant in conjunction with the poor return would result in a loss. It is obvious that waste heat recovery in the wet process can only be seriously considered in the case of forced rotary kilns. It has been stated in America that " the entire power for running a cement works can be won from the waste heat of the rotary kiln "; it is proposed to examine the promised advantages of waste heat recovery by means of the data given in the preceding articles. To obtain comparable results a basis on which the calculations are made must be established.

A steam pressure of 20 atmospheres and temperature of 350 deg. C. are assumed for the waste heat plant, consisting of superheater, boiler and economiser. One kg. steam thus contains 740 kcal. Since the kiln gases—especially in the wet process—contain large quantities of steam, together with cement dust, the " sweating " of the economiser must be prevented by preheating the feed water before it enters the economiser. In the dry process a temperature of 40 deg. C. is sufficient; in the wet process, with $b_{max} = 40$ per cent., 70 deg. C. Thus 1 kg. steam corresponds to the transfer of 700 kcal. in the dry process and 670 kcal. in the wet process. The heat required to raise the feed water temperature, which is obtained from the waste steam of the feed pumps or engine, is not considered in the calculations.

Tables XV and XVI (CEMENT AND CEMENT MANUFACTURE, April, 1932) are calculated for an excess air factor $\lambda = 1.2$. Even under the most careful control of a waste-heat boiler plant it is impossible to avoid the entry of additional air into the kiln gases. Table XXVI gives the results of experiments in the U.S.A. in which the CO_2 was determined before the gases entered the waste-heat boiler, and at the fan behind the boiler.

It will be assumed in the calculations that λ increases from 1.2 to 1.8 between entering the waste-heat plant and leaving the economiser. The loss from the boiler plant by radiation, conduction, and convection is taken to be 3 per cent. of the available heat in the gases entering the boiler.

In waste-heat recovery, assuming 200 deg. C. to be the final temperature of the waste gases, the natural chimney draught is insufficient, and an exhaust-fan must be used. Table XXVI gives the draught in the kiln, before and after the gases pass through the waste-heat plant, in the various United States works considered. Since it is necessary to move considerable volumes of gas, while the velocity of the gas over the heat exchange surfaces must be high, to reduce

TABLE XXVI.

Variation of Excess Air Factor and Draught in Waste-Heat Plants in the United States.

Plant. No.		1.	2.	3.	4.	5.	6.
Fuel consumption, x. ....kg.		226	280	250	269	263	256
In front of waste-heat boiler.	CO_2 .... per cent.	28.8	21.0	26.5	25.0	28.5	28.0
	λ	1.03	1.36	1.10	1.15	1.00	1.03
	Draught, mm. water gauge	7	18	11	7	17	10
At the fan	CO_2 ....per cent.	14.9	13.0	14.0	17.0	13.6	17.0
	λ	2.20	2.25	2.20	1.75	2.20	1.80
	Draught, mm. water gauge	98	125	170	208	270	100

the area and cost, we must work with a pressure difference of at least 100 mm. water gauge at the exhaust-fan. Assuming the fan efficiency to be 62 per cent. and the loss between fan and generator 20 per cent., 0.55 kWh must be taken from the generator per 1,000 cu. metres of gas passing the fan. This power consumption forms part of the losses that are essential in the process of heat recovery.

The conditions in the power plant are those already stated in this journal for June, 1932, and the steam consumption is 6.0 kg. per 1 kWh of power developed. On this basis the data for the dry process given in Table XXVII are obtained.

TABLE XXVII.

Waste-Heat Recovery in the Dry Process.

Coal consumption, x	kg.	200	220	240
Heat available in kiln gases	kcal.	662,660	797,660	935,660
Waste gas temp. t_o ($\lambda = 1.2$, $b = 10$).......	deg. C.	715	810	870
Loss in boiler	kcal.	19,880	23,930	28,070
Final loss in gases ($\lambda = 1.8$, 200 deg. C.)....	,,	233,640	253,025	272,410
Gross gain in steam......................	,,	409,140	520,705	635,180
Efficiency of boiler plant	per cent.	61.8	65.3	68.0
Quantity of steam	kg.	584.8	746.8	907.4
Gross power gained	kWh.	97.5	124.4	151.2
kg. steam per kg. powd. coal..............	kg.	2.93	3.4	3.8
Volume of gas ($\lambda = 1.8$, 200 deg.)..........	cu.m.	6,300	6,840	7.375
Power consumed by fan	kWh.	3.5	3.8	4.1
Power consumed by fan	kcal.	14,600	15,800	16,950
Net gain	kWh.	94.0	120.6	147.1
Net gain	kcal.	394,540	504,505	618,230
Heat requirement of 1,000 kg. clinker, including all losses, but deducting the net heat recovered in the steam	kcal.	1,105,460	1,145,495	1,181,770

From this Table can be obtained the coal consumption of the rotary kiln, x, which must be adopted in order to develop the entire power requirements of the cement works from waste-heat recovery. According to Table XXIII (Cement and Cement Manufacture, June, 1932) the average power consumption, exclusive of coal grinding, is 99 kWh per 1,000 kg. clinker. To this must be added the power consumed in grinding the coal. If both kiln and raw material drier

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are coal-fired $(30+x)$ kg. of powdered coal must be produced, for which is required $(30+x) \times 0.04 = (1.2+0.04x)$ kWh.

The curve (a) of Fig. 15 gives the power consumption $(99+1.2+0.04x)$. Curve (b) gives the net gain from waste-heat recovery in kWh. The intersection of the two curves gives the value of x for which the entire power consumption can be covered by waste-heat recovery; this value is $x = 211.1$ kg. Thus the overall fuel consumption of the works, including power production, is

Raw material drier	30.0 kg.
Rotary kiln	211.1 ,,
Coal drier	2.6 ,,
Total	243.7 ,,

If x_t be the total powdered coal consumption of a cement works having a power plant with direct coal firing, then x_t is composed as follows:—

Raw material drier	30.0 kg.
Rotary kiln	x kg.
For power consumed exclusive of coal grinding ..	0.792×99 kg.
For grinding coal used by kiln and drier	$0.04 \times 0.792(x+30)$ kg.

$$x_t = 30.0 + x + 0.792 \times 99 + 0.04 \times 0.792(x+30) \text{ kg.} = 1.032x + 109.4.$$
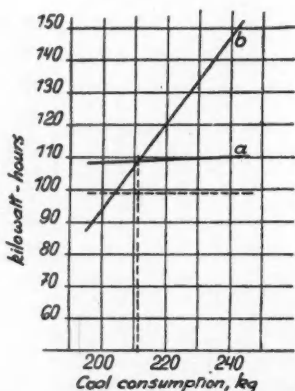
Fig. 15.—Graphs for finding the value of x in the dry process, such that the power requirement of the plant is just covered by waste heat recovery.

Fig. 16.—Waste heat recovery in a dry process rotary kiln.

By equating x_t with $(211.1+30.0)$ kg. we obtain the kiln fuel consumption, x, which must not be exceeded if a works without waste-heat recovery is to be as efficient as a works utilising waste-heat recovery. Thus

$211.1 + 30 = 1.032x + 109.4$; i.e. $x = 127.6$ kg., equivalent to 957,000 kcal.

The advantage of waste-heat recovery in the dry process is obvious from the point of view of heat economy in the case of works which must produce their own electricity. Fig. 16 gives the Sankey diagram for the distribution of heat in the rotary kiln and waste-heat boiler for $x = 211.1$ kg., assuming a clinker output of 200 tons per 24 hours.

TABLE XXVIII.

Waste Heat Recovery in the Wet Process.

Water content of slurry... per cent.	36			38			40		
Coal consumption, x ...... kg.	280	300	320	280	300	320	280	300	320
Heat available in kiln gases kcal.	824,500	973,000	1,124,500	778,750	927,250	1,078,750	728,770	877,270	1,028,770
Waste gas temp. t_g (λ = 1.2) deg. C.	550	620	675	510	575	640	460	530	595
Loss in boiler.......... kcal.	24,735	29,190	33,725	23,360	27,820	32,360	21,860	26,320	30,860
Final loss in gases (λ = 1.8, 200 deg. C.)........ „	376,365	395,750	415,135	383,475	402,860	422,245	391,340	410,725	430,110
Gross gain in steam ...... „	423,400	548,060	675,630	371,915	496,570	624,145	315,570	440,225	507,800
Efficiency of boiler plant.. per cent.	51.3	56.3	60.0	47.8	53.5	57.9	43.3	50.0	56.2
Quantity of steam........ kg.	632	818	1,008.4	555	741	931.5	471	657.4	847.4
Gross power gained....... kWh.	105.2	136.3	168.1	92.5	123.5	155.8	78.5	109.6	141.2
kg. steam per kg. powd. coal .... kg.	2.0	2.5	2.9	1.8	2.3	2.7	1.5	2.0	2.5
Volume of gas (λ = 1.8, 200 deg.) ...... cu. m.	9,950	10,500	11,120	10,100	10,650	11,200	10,300	10,850	11,400
Power consumed by fan .. kWh.	5.5	5.8	6.1	5.6	5.9	6.2	5.7	6.0	6.3
Power consumed by fan .. kcal.	22,000	23,200	25,000	22,400	23,600	24,700	22,600	24,000	25,200
Net gain .... kWh.	99.8	130.5	162.0	86.9	117.6	149.6	72.8	103.6	134.9
Net gain .... kcal.	401,400	524,800	650,630	349,515	472,970	599,445	292,970	416,225	542,600
Heat requirement of 1,000 kg. clinker, including all losses, but deducting the net heat recovered in the steam .... kcal.	1,698,600	1,725,140	1,749,370	1,750,485	1,777,030	1,800,555	1,807,030	1,833,775	1,857,400

Table XXVIII gives the heat recovery data for the wet process with different percentages of water in the raw-material slurry. Taking N kWh as the power consumption of the cement plant, exclusive of coal grinding, the following expression is obtained for the total powdered coal consumption, x_t, of a works without waste-heat recovery but with its own power plant:

$$x_t = x + 0.792N + 0.04 \times 0.792x = 1.032x + 0.792N.$$

If x in this equation be varied from 200-240 kg., a family of curves connecting x_t and N results as in Fig. 17. Fig. 17 also shows the net power gained by waste-heat recovery (from Table XXVIII), reduced by $0.04x$

For waste-heat recovery $x_t = x$. Fig. 17 gives a direct comparison of working with and without waste-heat recovery, and clearly shows that in the wet process:

(1) The value of waste-heat recovery is greatly dependent on the water content of the raw material slurry, b; this fact offers the possibility of future improvements.
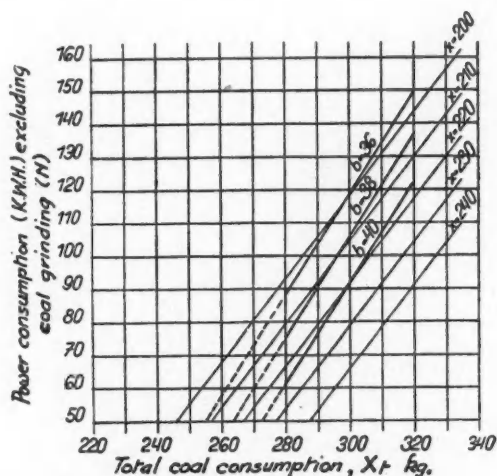
Fig. 17.—Total coal consumption in wet process,
with and without waste heat recovery.

(2) The advantage to be reaped from waste-heat recovery depends on the minimum coal consumption of the rotary kiln. In Tables XIX to XXI this is taken as $x = 240$ kg., a value which can be maintained, although it requires the greatest care on the part of the kiln attendant and the management. Taking $x = 240$ and N = 90 kWh. in Fig. 17, a total coal consumption $x_t = 319$ kg. is obtained without waste-heat recovery, and $x_t = 299$ kg. with recovery, using a slurry of 40 per cent. water content. The economy in fuel is thus 20 kg. per 1,000 kg. clinker, or 6.27 per cent., with waste-heat recovery. If the slurry contains 36 per cent. water, x_t is reduced to 281 kg., and the economy resulting from waste-heat recovery increases to 11.9 per cent. The advantage to be gained from waste-heat recovery increases as the water content of the slurry is reduced. Further, the higher the value we are compelled to assign

to the minimum fuel consumption of the kiln, the greater will be the gain from waste-heat recovery.   Considering, then, the kiln fitted with chains described in Part III (CEMENT AND CEMENT MANUFACTURE, April, 1932), or the Rigby process, whereby the coal consumption of the wet process can be reduced to $x = 220$ kg. or less, waste-heat recovery can be of no interest in the case of raw materials which do not permit of the production of a slurry of low water content.   On the other hand, filtration of the slurry, where feasible, offers the possibility of adopting waste-heat recovery in the wet process with results approaching those obtained in the dry process.

In general, it may be said of waste-heat recovery in the rotary kiln that it entails coupling two separate plants which are intrinsically unrelated and which in many ways oppose each other.

The preceding considerations are based on the average power consumption of cement works.   However, the variations in load during the course of a day can be of considerable importance, particularly in modern works which consist of only a few large machine units.   The preliminary crushing plant for the raw materials is an instance of this, since it must accommodate itself to the quarry and work a shift of only eight hours in twenty-four.   Any starting or stopping of the large grinding mills has a still greater effect on the power-generating plant.   With a view to the regular running of the kiln, the power plant must be loaded as uniformly as is possible.   Where this is not practicable it is desirable not to increase the output of the waste-heat boiler to give the variable portion of the power required, but to run a separate directly fired subsidiary boiler for this purpose.   Otherwise a waste of fuel results which is very apt to continue permanently.   In cases where a varying load is required the waste-heat boiler may also be assisted by subsidiary firing with oil or gaseous fuel, so that control of the kiln is independent of fluctuation of the load on the power plant.   Powdered coal is less satisfactory for such subsidiary firing on account of the ash.

It is usual in almost all European cement works to run only the kiln on Sundays, with the minimum of accessory plant.   The installation of a waste-heat boiler, however, makes it desirable to recover the heat from the waste gases on Sundays as well as week-days, but the working of the complete plant on Sunday will have the disadvantage of increasing the average rate of wages, while it will not always be possible to undertake Sunday working.

Among the possible disadvantages of forcing the rotary kiln is the effect of the fuel ash on the quality of the clinker, particularly when the coal to be used is high in ash.   On the other hand, over-burning the clinker need hardly receive consideration; the only effect of a sharply burnt clinker in the case of a forced kiln with waste-heat boiler is to increase the power required for grinding, as a result of the increased hardness of the clinker.

In the case of old works with out-of-date mechanically driven plant, which is yet capable of many years' service, the introduction of waste-heat recovery will in many instances show a clear economy, even in the wet process, over the old-fashioned power-wasteful method.   The calculations can be accurately adapted to the particular conditions by basing them on measurements made on the plant, and if they are adequately carried out they can be made to cover all the daily variations of conditions.   The decision in favour of waste-heat recovery will more easily be taken if the works already develops its own power. The original boiler plant can be used after the installation of the waste-heat boiler to cover the peak load on the generator, so that there is no need to force the waste-heat boiler and disturb the running of the kiln.

The decision as regards installing waste-heat recovery plant is much more difficult to make in the case of a new cement works; there are then two major possibilities:

(1) Electricity must be generated in the works' own power plant.

(2) Electricity can be obtained from an outside supply.

In the first case the following questions must be answered:

(a) What is the increased capital cost of installing a waste-heat boiler as against a separate directly-fired boiler for power generation?

The waste-heat boiler will be considerably more expensive, since its output per square metre of heating surface is 8 to 10 kg. steam per hour for the dry process and 6 to 7.5 kg. for the wet process; with the directly-fired boiler the specific steam output is at least 30 kg. Thus the heating surface of the waste-heat boiler must be at least three to five times greater than that of a separate boiler, assuming equal steam output. Greater heating surfaces are also necessary in the superheater and economiser.

(b) What are the relative fuel costs of the two processes?

In answering this question it should be assumed that the minimum practical fuel consumption, x_{min}, will be attained. As has already been indicated, various modern developments in the wet process render the adoption of waste-heat recovery a matter for serious consideration. As regards the dry process, results with a relatively small experimental plant have proved that the Polysius-Lellep process gives results practically equal to waste-heat recovery.

(c) To what extent are these practical disadvantages to waste-heat recovery due to the amalgamation of two intrinsically different plants?

It is impossible to form a generally valid opinion on this question. It would be wrong to apply the favourable results given by waste-heat boilers in existing plants to new cement works without criticism, and it would be equally wrong to base the decision entirely on a calculated comparison of the heat values.

When an external electricity supply is available the price of supply must be considered in conjunction with the foregoing points. The tendency to concentrate power generation in a few favourably located centres will in future facilitate the supply of electricity and react against the construction of power generating plants in individual new cement works.

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Cement in French Indo-China.

Soc. des Ciments Portland Artificiels de l'Indo-Chine report a decrease of 30 per cent. in sales for the year 1931 compared with 1930, chiefly due to decreased demand on the home market. Haiphong, one of the company's two works, is being rebuilt and will be completed during the second half of 1933. During February this year the Company reports record delivery figures owing to the Russian and Chinese boycott of Japanese goods. The profit for the year 1931 was 6,231,579 francs (£50,170) and the dividend 20 francs, compared with a profit of 9,600,000 francs and a dividend of 30 francs in 1930.

Cement Production in Canada.

The production of Portland cement in Canada for the four months, January to April, 1932, amounted to 1,210,151 barrels, compared with 2,205,131 barrels for the same period last year.

Studies of Portland Cement in Relation to the Disintegration of Concrete.

PAPERS by Professor R. J. Colony, of Columbia University, and Professor D. L. Snader, of the Stevens Institute of Technology, published in a Bulletin of Columbia University, give the results of their investigations into the constitution of Portland cement and the properties of cement components in relation to the disintegration of concrete.   The deterioration of concrete under service conditions has been studied both in the field and in the laboratory. The field inspection covered numerous concrete structures in various stages of deterioration ranging from incipient to advanced and, wherever permission could be obtained, representative samples of deteriorated concrete were cut out. These samples were studied and tested, the tests including the determination of the physical properties of the concrete, a microscopic examination of thin sections, and sometimes a chemical analysis.

The studies showed that in general the disintegration of concrete is confined to the complex hydrated cement matrix, the so-called binder. Disintegration of the binding material was found most pronounced in structures exposed to contact with water, and deterioration is most marked in places where the evaporation and percolation of water are most pronounced.   The authors state that low physical properties of the concrete as affected by mechanical conditions of manufacture, such as proportions and quality of aggregates, mixing, placing and curing, are very important contributing factors, but not essentially primary ones in retarding or preventing the deterioration of concrete. Nevertheless, the object in making and placing concrete should be to secure as watertight and impervious a concrete as it is economically possible to produce.   Some of the products of hydrolysis of all commercial Portland cements are chemically unstable to the extent that they may undergo complete hydrolysis in the presence of water with the production of gelatinous silica and alumina and calcium hydrate. With the water confined in the interstices of the concrete, hydrolysis ultimately ceases as the water becomes saturated with the soluble products resulting from hydrolysis; on the other hand, with water percolating through the mass hydrolysis continues slowly until it has been carried to completion or nearly so. The papers do not deal with the deterioration and disintegration of concrete resulting from mechanical abrasion or wear or the action of frost.

An investigation of the causes of the disintegration of concrete masonry involves primarily a study of the constitution of Portland cement and its hydration products. Such a study should include the determination of the physical properties and the chemical stability in water of the products of hydration. All of this has been done by preparing and testing artificially prepared and chemically pure hydrated components of Portland cement. Studies both microscopic and by means of X-rays have been made to determine the major hydrated constituent components of Portland cement in the samples of concrete removed from existing structures in various stages of disintegration.   The physical properties of the concrete in these samples have also been determined.

The following is a summary of Professor Colony's paper, entitled " The Products of Hydration and Hydrolysis of Portland Cement ":

(1) The two major crystalline components of Portland cement appear to be dicalcium silicate and tricalcium silicate. The tricalcium silicate contains many

crystal inclusions which may possibly contain part of the alumina in some form. A third complex and variable slag-like and indeterminable dark-coloured interstitial mass acts as another component. Most of the iron, and perhaps alumina, with both lime and silica (complex slag?) make up this component, which behaves as a matrix in which the two major crystalline components are distributed. Tricalcium aluminate as such could not be definitely identified, although, if all the alumina in normal Portland cements were present in that form, from 12 to 20 per cent. of the cement would consist of a quantity of tricalcium aluminate which should be readily identified in cement clinker.

(2) The two calcium silicates hydrolyze with the formation of the same products of hydrolysis, calcium hydrate and hydrated gel-like calcium silicate. Tricalcium silicate hydrolyzes much more readily, yielding more calcium hydroxide in the process than dicalcium silicate. The " third " indefinite component hydrolyzes also, producing hydrated products carrying both iron and alumina.

(3) The marked rapid disintegration of test-pieces made of tricalcium aluminate when immersed in water indicates that tricalcium aluminate as such may not exist as one of the important components of Portland cement. The alumina may occur in another form; perhaps in the " third " complex component as suggested. It does not seem logical that from 12 to 20 per cent. of tricalcium aluminate in cement should be so modified in behaviour by reason of fine intercrystallization with the other components that it would exert no destructive action in cement, even when neat test pats are subjected to boiling.

(4) When concrete structures are subjected to intermittent, or constant slow and long-continued, percolation of water, as in a dam, the components of the cement may completely hydrolyze, because the continued removal of one of the products of hydrolysis (calcium hydroxide) by solution and precipitation as crystalline calcium hydroxide, or as calcium carbonate, permits the action to go on; and under such conditions concrete frequently softens and disintegrates.

(5) Standard Portland cements differ in chemical composition within very narrow limits; consequently they all contain the same components. The components vary in proportions in different cements, the variation being dependent on the narrow range of variability in chemical composition. The products of hydrolysis of all Portland cements are accordingly substantially the same, but they, likewise, differ in proportion; and perhaps the degree of hydrolysis will differ dependent on factors connected with making, mixing, and placing the concrete of which the cement is one ingredient.

Professor Snader's paper is entitled " Physical Properties and Characteristics of Tricalcium Silicate, Dicalcium Silicate, Tricalcium Aluminate and Dicalcium Ferrite." It is summarised as follows:

Tricalcium Silicate.—(a) Tricalcium silicate requires a minimum of 58 per cent. of its own weight of mixing water to reduce it to normal consistency.

(b) There is no rise in temperature after addition of the mixing water and no flash set occurs, but it possesses a striking characteristic of " settling down " during mixing and placing in moulds.

(c) The small test cylinders could be safely removed from the moulds at the end of two days, so that the rate of setting and hardening is not as rapid as for tricalcium aluminate or dicalcium ferrite, but much more rapid than for dicalcium silicate.

(d) For ages up to six months no volumetric changes occurred during curing in the damp closet, and no checking or cracking could be detected under a magnification of 14X.

(*e*) Tricalcium silicate increases steadily in strength with age, and at the age of six months it has the highest compressive strength of any of the compounds.

(*f*) After nine months' immersion in water the soundness and structural stability of cylinders of hydrated tricalcium silicate do not appear to be affected. No crazing or cracking could be detected under a magnification of 14X, and the compressive strength was 7,600 lb. per sq. in.

(*g*) As early as two days after immersion in water crystals of calcium carbonate appear on the surface of the cylinders indicating the presence and liberation of lime in the hydrated mass, and after nine months' immersion in water these crystal formations of calcium carbonate became profuse and could easily be removed from the cylinders in large convex pieces and sheets.

(*h*) A small increase in volume was found from absorption when small cylinders of tricalcium silicate were immersed in water with a maximum of 1.36 per cent. for cylinders immersed for 37 days in water.

(*i*) The percentage of water absorbed varied with the age of the cylinders before immersion and was found to average 26.6 per cent. absorption for immer-
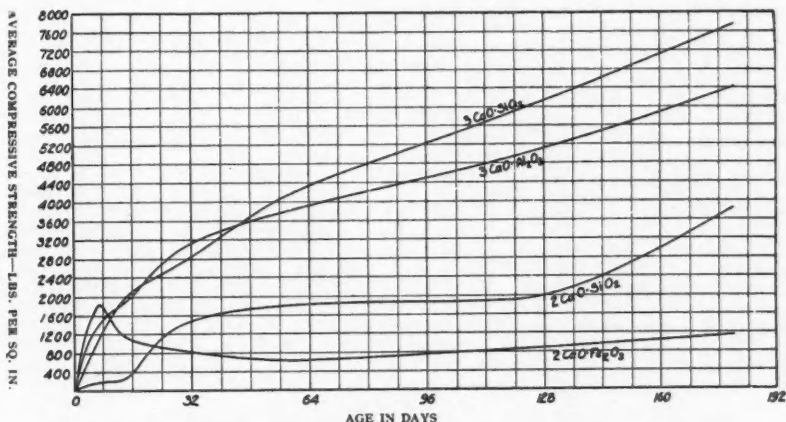
Average Compressive Strength of Tricalcium Silicate, Dicalcium Silicate, Tricalcium Aluminate, and Dicalcium Ferrite.

sion for 37 days and aged 120 days in the damp closet before immersion. Absorption was most rapid during the first 15 to 30 minutes.

(*j*) Tricalcium silicate appears to be the most valuable component of Portland cement. It sets and hardens rapidly, does not undergo volumetric change during storage in the damp closet, remains sound, and has high enduring qualities under severe conditions of exposure. Its compressive strength is relatively high and increases with age.

Dicalcium Silicate.—(*a*) A minimum of 27 per cent. of its own weight of mixing water is required to produce normal consistency.

(*b*) There is no rise in temperature after the addition of the gauging water, no flash set occurs, and no remixing is required during placing in the moulds.

(*c*) It sets and hardens very slowly; the small cylinders could not be safely removed from the moulds until seven days after moulding, and even then great care was required to guard against breakage.

(d) The setting, hardening, and increase in strength are very slow, gradual and continuous for a long period of time.

(e) Hydrated dicalcium silicate is more granular in texture than any of the four compounds studied, and the cylindrical surfaces are somewhat powdery and chalky and do not become smooth and glassy.

(f) For ages up to six months no volumetric changes occurred during curing in the damp closet, and no crazing or cracking could be detected under a magnification of 14X.

(g) At the age of seven days dicalcium silicate has the lowest compressive strength of the four compounds. It increases in strength slowly with age, and at the age of six months its compressive strength is only 60 per cent. of that of tricalcium silicate.

(h) After nine months' immersion in water the soundness and structural stability of cylinders of hydrated dicalcium silicate do not appear to be affected at all. No crazing or cracks could be detected under a magnification of 14X, and the compressive strength was 4,250 lb. per sq. in.

(i) Crystalline deposits of calcium carbonate form on the surface of the cylinders when immersed in water, which dissolves and liberates lime from the hydrated mass. After nine months in water these crystalline surface deposits are pronounced and could be removed only with considerable difficulty and then only in powdery form, but they are not as profuse and not as definite in appearance as the crystals of calcium carbonate that form on the surfaces of cylinders of hydrated tricalcium silicate when immersed in water.

(j) Only a very small increase in volume was found from absorption when cylinders of dicalcium silicate were immersed in water. An increase in volume of 0.79 per cent. was found for cylinders immersed nine months in water.

(k) The percentage of water absorbed was less than that for tricalcium silicate, and varied little with the age of the cylinders before immersion. The absorption for cylinders immersed for sixteen days in water and aged 180 days in the damp closet before immersion averaged 17.7 per cent.

(l) Dicalcium silicate appears to be a valuable compound in Portland cement, even though it is slow setting, has low early compressive strength and slow increase in strength with age. It does not undergo volumetric change during ageing in the damp closet, remains sound, and has high enduring qualities under severe conditions of exposure.

Tricalcium Aluminate.—(a) A minimum of 60.5 per cent. of its own weight of mixing water is required to produce normal consistency.

(b) A striking rise in temperature occurs immediately after the addition of the mixing water, and continues during the first twelve minutes, after which there is a gradual decrease in temperature.

(c) Another striking characteristic is the rapid initial set (a flash set) which requires extremely rapid placing in the moulds. Three or four minutes after completion of mixing, remixing without the use of additional water is required so that placing in the moulds may be completed.

(d) Hydrated tricalcium aluminate sets and hardens rapidly; the small cylinders can be safely removed from the moulds after 24 hours.

(e) A small increase in volume occurs during the first two weeks of curing in the damp closet, during which time the volume appears to become practically constant.

(*f*) A small number of longitudinal and transverse cracks developed in all cylinders soon after moulding and during storage in the damp closet.   These were observed under a magnification of 14X as early as 23 hours after moulding.

(*g*) At the age of seven days tricalcium aluminate has the second highest compressive strength.   It continued to increase in strength with age during the time covered by the tests, and at the age of six months its compressive strength was 82 per cent. of that of tricalcium silicate.

(*h*) Cylinders of hydrated tricalcium aluminate when immersed in water begin to disintegrate almost immediately.   Disintegration proceeds rapidly until in some cases the cylinder in about ten days is often reduced to mud which with small pieces and fragments of the original cylinder embedded in it collects in the bottom of the vessel.   At the same time thick coatings of calcium carbonate collect on the surface of the water and on the sides of the glass vessel.

(*i*) A large increase in volume was found when small cylinders of hydrated tricalcium aluminate were immersed in water; this amounted to 14.85 per cent. for cylinders immersed for 26 days in water.   The increase in volume is rapid during the first four hours, when it amounted to 10.26 per cent.

(*j*) The percentage of water absorbed was found to be large and extremely rapid, and amounted to 15.7 per cent. during the first 15 minutes' immersion in water.

(*k*) Tricalcium aluminate has the valuable property of setting and hardening rapidly and has a relatively high compressive strength; but under the action of water it undergoes a large increase in volume and disintegrates rapidly and completely.   Tricalcium aluminate may not exist as a component of Portland cement, or if it does occur as one of the components, it must be present only in small percentages.   From the characteristics, properties and action found for hydrated tricalcium aluminate it is difficult to see how it could exist in any appreciable quantity as a component of cement without being very detrimental to the concrete made with such cement.

Dicalcium Ferrite.—(*a*) A minimum of 24.5 per cent. of its own weight of mixing water is required to produce normal consistency.

(*b*) There is no rise in temperature after addition of the mixing water, no flash set, and no remixing is required during the time of placing in the moulds.

(*c*) The mixed material is somewhat " pasty " and " gluey."

(*d*) Hydrated dicalcium ferrite sets and hardens rapidly.   The small cylinders could be safely removed from the moulds 22 hours after placing.   Two hours after placing the hydrated material in the moulds, the cylinders are harder than those of dicalcium silicate at the age of two to three days; and three hours after placing they are as hard as those of dicalcium silicate at the age of five to seven days.

(*e*) Cylinders of hydrated dicalcium ferrite increase very greatly in volume during curing in the damp closet.   This increase in volume was continuous over the entire period of observation of six months, and about three-fourths of it occurred during the first month.

(*f*) Numerous cracks and crazing developed in all cylinders almost immediately following moulding, and during storage in the damp closet.   These are coincident with and related to the great increase in volume.   They were definitely visible at the age of 22 hours and continued to grow and expand during the entire period of observation of six months.   At the age of 14 days they penetrate very deeply into the cylinder, apparently to its centre.

(*g*) The cracking extends throughout the entire mass, and cylinders subjected to compression break into many small pieces somewhat uniform in size.

(*h*) At the age of seven days dicalcium ferrite has the greatest compressive strength of the four compounds. It decreases in strength with age up to about two months, after which there is a small increase in strength. At the age of six months its compressive strength is the lowest of all of the four compounds, and is only 15 per cent. of that of tricalcium silicate.

(*i*) The disintegration of cylinders of hydrated dicalcium ferrite is accelerated by immersion in water. After two to three hours' immersion in water the condition is about the same as the condition after four to six months' storage in the damp closet. Actual falling apart of the cylinder begins within about one hour after placing in water, and the breaking up is fairly complete in from two to six days of immersion in water.

(*j*) A large increase in volume was found when small cylinders of hydrated dicalcium ferrite were immersed in water. The percentage increase during the first four hours is only about one-fourth as much as for tricalcium aluminate, but it is continuous over long periods of time. An increase in volume of 36.14 per cent. was found for cylinders immersed 50 days in water and previously aged 14 days in a damp closet.

(*k*) The percentage of water absorbed by cylinders of hydrated dicalcium ferrite was found to be high and very rapid. It was found to average about 11.0 per cent. after the first 15 minutes' immersion in water.

(*l*) Dicalcium ferrite is volumetrically the most unstable of the four compounds studied. Along with the large increase in volume of cylinders of hydrated dicalcium ferrite, disintegration results from the formation of numerous cracks and crazing during curing in the damp closet. The increase in volume and disintegration are greatly accelerated by contact water. The characteristics, properties and action of hydrated dicalcium ferrite appear to be such as to make it a detriment as a component of cement. From the results of the study, dicalcium ferrite is not a normal component of Portland cement.

New Russian Cement Plant.

The U.S.S.R. has decided to erect a cement factory in the Orsk district at a cost of £1,500,000.

New Japanese Cement Plant.

It is reported that the Asano Cement Company is considering the erection of a new cement plant at Kirin, Japan.

The Mexican Government and the Cement Industry.

The state of Hidalgo, Mexico, has announced that it has taken over the Cruz Azul cement plant, the first private property expropriated under a new law which came into effect on May 1, under which a State Governor is authorised to take over any property believed to be needed by the state. It is reported that the owners of the plant are contesting this decision.

Cement Production in the United States.

For the five months, January to May, 1932, the total production of Portland cement in the United States was 26,239,000 barrels, compared with 46,000,000 in 1931 and 59,000,000 in 1930. For the twelve months ending May, 1932, the percentage of production to capacity was 38.9, against 56.5 in 1931 and 66.2 in 1930. For the month of May only production was 30.2 per cent. of capacity.
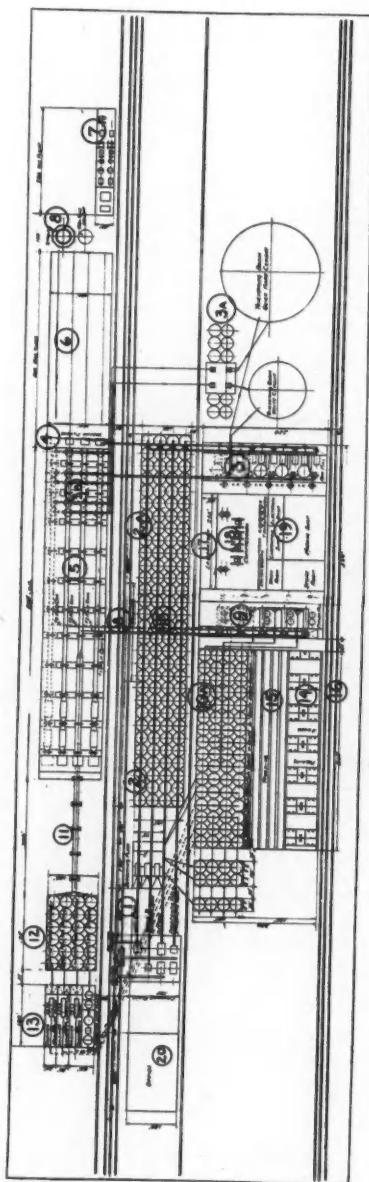
Design for a Modern Cement Plant.

IN a recent number of "Pit and Quarry," Mr. Aman Moore gives a design for the layout of a super plant designed to produce super-quality cement at minimum cost. The plant is designed to manufacture quick-hardening Portland cement, white cement, marine cement, gypsum products, magnesite products, complete fertiliser products, raw and burned lime products, and gas-ice as a by-product.

The crushing plant (marked 1 in the drawing) includes a primary gyratory crusher large enough to receive a rock at least 5 ft. by 7 ft. A large electrical steam shovel, having a dipper of not less than 6 cb. yd. capacity, loads directly into railway trucks, which are dumped into the crusher by overturning them in a tumbler directly over the crusher. The rock passes over a grizzly, the residue from which goes to the secondary crusher. From here part of the rock used for cement manufacturing goes directly to concrete storage-silos (2 and 2A) 30 ft. in diameter by 90 ft. high. The rest passes over rolls, where it is graded to supply various products, including lime dust, chicken grit, pebble dash in $\frac{1}{4}$ in. to $\frac{1}{2}$ in. sizes, and rock in $\frac{3}{4}$ in. to $1\frac{1}{2}$ in. sizes, and in 3 in. to 6 in. sizes for sugar manufacturing. The same flow-line is followed for crushing magnesite rock, gypsum rock, phosphate rock, and shales for the cement mix. Different concrete silo storage tanks are used for the various kinds of crushed products.

In the operation for which this layout was designed two types of shale, one a feldspatic rock high in aluminium and the other a shale very high in iron, are used. These materials are also crushed separately and stored in separate concrete silos. The crushed lime rock and the high-aluminium and high-iron shale are drawn from the concrete storage silos and passed on to hoppers over the raw-grinding mills (3). Each type of shale and lime rock is ground in separate grinding mills, which employ the closed-circuit system and use thickening basins (3A), or the material passes directly into storage tanks (3B) at the back end and under the kilns. In the storage and correction tanks a proper mix of the slurry is made, and after the mix has been corrected it passes on to vacuum filter presses (4), where the water content is reduced and where the filter-cake when entering the back end of the kiln contains approximately 18 per cent. of water.

In determining the length of the kilns (5) efficiency of fuel and low temperature of stack gases are the main guiding factors. It is planned to line the entire length of the kilns with fire-brick, using at least 1 in. of fireproofing cement between the kiln-lining brick and the kiln shell. The object is to prevent, as nearly as possible, the radiation of heat through the kiln shells. Using a kiln length of 800 ft., the stack temperatures are approximately 425 deg. F., at which temperature the gases can be passed through woollen bags in the bag-house (6) installed directly behind the kilns. By the time the gases have passed through the meshes of the woollen bags in the bag-house, which is 500 ft. in length, the temperature of the gases is reduced to approximately 225 deg. F. Practically all solids in the gases, including waste dust from cement materials, volatilised potash, etc., should be removed. By the time the gases have been drawn by fans from the farther end of the bag-house they are in proper condition to enter the gas-ice recovery plant (7), or if a surplus of the cool cleaned kiln gases should occur it can be forced up the stack (8).

A double set of soaking zones is provided for kilns No. 1 and No. 3. In kiln No. 1 it is planned to manufacture 3,000 barrels daily of white cement, and in kiln No. 3, 6,000 barrels per day of quick-hardening Portland cement with only one burning. The back section of kiln No. 1 is 9 ft. in diameter and the soaking

Layout of a Modern Cement Plant.

zones 11 ft. 6 in. in diameter. The back end of kiln No. 3 is 11 ft. 6 in. in diameter, and the soaking zones in front 15 ft. in diameter.

Kiln No. 2 is 600 ft. long and 9 ft. in diameter, the front 200 ft. being an enlargement to 11 ft. 6 in. in diameter. Soaking zones are not provided in kiln No. 2 because this kiln is used to manufacture marine or high-iron cement part of the time and then alternately to calcine, separately in the rock form, magnesite, gypsum, phosphate rock, and limestone.

Each kiln is provided with a cooler doubling back from the discharge end to separate belt-conveyors (8). The coolers are approximately 320 ft. long and 9 ft. in diameter. A sealed stationary hood prevents cold air from entering between the discharge end of the kiln and the cooler, so that all the air entering the kiln is preheated to a temperature of 1,000 deg. F., or more. When the clinker is discharged to the conveyors it should be so cool that no difficulty would be experienced in handling it in the naked hand. The clinker passes to cement-grinding mills (9), a separate grinding mill for each of the three types of cement to be delivered. These grinding mills are of the closed-circuit type. Each has four compartments, and is constructed so that each compartment empties completely at the end of the compartment, the product passing over air-separators and only the coarse materials passing on to the next compartment. By this method the fines are removed from the coarse particles, so preventing the formation of a cushion that reduces the efficiency of the grinding balls approximately 50 per cent. In other words, a mill of this type is presumed to give approximately double the capacity and to grind much more finely with the consumption of approximately the same h.p. as other types of tube and compartment mills.

When the hoppers over the grinding mills are full the cement clinker is stored in clinker storage-bins (10), and the conveyors (8) pass at right angles over the tops of the raw-material conveyors leading from the same bins, conveying raw materials from the crushing plant. All the storage bins can be used either for clinker or for any one of the several kinds of raw crushed rock and shale. All the storage-bins are provided with hopper bottoms, and have conveyors underneath them for emptying the bins and returning the product either to clinker-grinding mills or to raw-grinding mills.

The different brands of cement are pumped from the grinding mills (9) to the storage tanks (10A), which are constructed in the same manner as those shown at 2, 2A and 10, and have a diameter of 30 ft. and a height of approximately 90 ft.

Kiln No. 2 is provided with a second cooler (11) which extends directly in front of the discharge end of the kiln and is of approximately the same length and size as the other coolers, which double back underneath the three kilns. As the different raw materials—crushed magnesite rock, crushed gypsum rock, crushed phosphate rock, and crushed limestone—pass through kiln No. 2 separately for calcining, it is planned to empty the kiln and the cooler after calcining one type of rock and before calcining another type of rock. It is because of this change from one type of material to another that kiln No. 2 is not provided with soaking zones.

Kiln No. 2 also has a Dutch oven, or preheating furnace, constructed to prevent overheating by direct contact of the raw gypsum rock with the flame while calcining. Each of the calcined materials—magnesite, gypsum, phosphate rock, and limestone—is discharged from the cooler to separate rows of storage silos (12), and from these they are drawn separately from underneath and passed on to separate plants (13) for grinding them. The calcined lime is passed through

hydrators.   These materials, after grinding and (in the case of lime) after hydrating, are pumped into separate rows of storage tanks in a part of the main storage plant (10A), alongside the silos containing the quick-hardening cement, white cement, marine cement, lime dust, chicken grits, etc.

The packing plant (14) has separate packers for each of the several products simultaneously.   These products can be loaded in trucks in the space provided for that purpose (15), or in railroad cars (16).   Above the packers for white cement provision is made for grinding with the white cement various coloured pigments so as to produce all the major coloured cements as well as white cement. Over the packers for plaster of Paris provision is made for adding retarder, fibre, etc., for producing hard wall plaster.   Over the packers for the calcined phosphate rock provision is made for adding nitrates, potash, raw-ground gypsum, or raw-ground lime to produce different types of complete mineral fertilisers.

The laboratory (17) is equipped with miniature plants for original research work, as well as physical and chemical laboratories for testing the raw and finished products.   The electrical room (18) contains compressors, transformers, switchboards, etc., and is connected with space wherein are the large motors operating the grinding mills for both raw and finished products.   Space (19) for the wash room, carpenter shop, electrical shop, storeroom and machine shop adjoins the electrical room and lies between the raw and finished-grinding departments.   The office (20) can be placed at whatever point may be found most convenient for entrance to the plant.

The plant is provided with a complete system of dust-collectors.   A hood of ample size is installed over each piece of machinery where dust is generated. The plant should be as clean as a city office building.   The economy resulting from the saving in waste more than pays the interest on the investment needed for the installation of a complete dust-collecting system, and the convenience to the mill operating force will be an additional asset.

All raw and calcined materials are handled only through closed storage tanks, which prevent the escape of dust or loss by wind, and also prevent depreciation in the quality of the product caused by exposure to rain when stored in the open.   All coarse materials are handled throughout the plant by belt-conveyor systems, and fine products by pumping by compressed air through pipe-lines.

The site of the projected plant is within the metropolitan district of one of the largest cities in the United States, where either gas, fuel oil, or slack coal is available through pipe-lines, thus eliminating freight charges for fuel.   It is contemplated to install, at a later date, crushing and grinding equipment at the quarry from which the ground slurry, containing between 50 per cent. and 90 per cent. of water, will be pumped through an 8 in. pipe-line to the plant.   By the use of such transportation of raw material the cost of delivering a ton of rock to the plant is reduced to only a few cents.

"The old system of locating numerous small plants at isolated points where limestone deposits exist should," states the author, "be a matter of history. A few large units should be constructed near or within the metropolitan districts of the largest cities of the United States.   The raw materials, ground to a fine slurry at the deposits, should then be pumped to the plants, situated where the market exists.   The fuel, too, should be piped to the plants.   A great saving in transportation cost, and hence a great reduction in the cost of producing and delivering a barrel of cement, would naturally result.   Furthermore, if single units including six pieces of machinery—one preliminary crusher, one secondary crusher, one closed-circuit raw-grinding compartment mill, one kiln, one cooler,

and one closed-circuit finish-grinding compartment mill—will produce 6,000 barrels each per day, then, with several of these units operating in one huge plant the operating costs can be greatly reduced. The quality of the product would be more uniform and more nearly perfect. Quick-hardening Portland cement manufactured under such conditions would cost considerably less than ordinary Portland cement of a quality inferior to that of super quick-hardening cements, which can be produced more perfectly and to greater advantage in modern super cement plants. It is my belief that if many of the cement factories in the United States were scrapped and a few super plants constructed near the largest cities a far better product would be supplied to the American cement consumer at a much less price than is available at present."

Algerian Cement Company's Dividend.

Soc. Nord Africaine des Ciments Lafarge has declared a dividend of 25 francs for the year 1931, when the net profit was 3,717,118 francs (£29,925), against 20 francs in 1930, when the profit was 2,144,995 francs (£17,270).

Proposed New Cement Plant at Tunis.

Under the title Ciments Artificiels Tunisiens, Tunis, a Société Anonyme has been constituted with a capital of 12,000,000 francs (£96,600) for the purpose of erecting a cement works in Tunis.

Proposed Australian Development.

The Queensland Cement and Lime Co. is seeking powers to transport coral and limestone from Moreton Bay to Oxley, where a crushing plant would be erected, and to pump it as a slurry to the works at Darra.

Wilson's (N.Z.) Portland Cement Co., Ltd.

The net profit of Wilson's (N.Z.) Portland Cement Co., Ltd., for the financial year ending in 1932 was £62,956, against £74,182 in 1931 and £89,955 in 1930. The dividend for each year has been at the rate of 10 per cent., but the bonus of 2½ per cent. distributed in 1930 and 1931 was discontinued for 1932.

The Cement Industry in Spain.

The report for the year 1931 of the directors of Cia. General de Asfaltos y Portland " Asland " states that cement consumption suffered a severe check due to the restriction of public works and the reduction of private building. This has obliged cement manufacturers to curtail production by about 50 per cent. Prices were not raised during 1931 except in cases where they were put up to the level of prices existing in 1928 and controlled at that time by the Junta Asesora. In order to reduce manufacturing costs it has been necessary to export in competition with cements from every source sold at " dumping " prices. Though the quantity exported (32,000 tons) does not represent a high percentage in total sales, it has been sufficient to cause a reduction in the average sales price of previous years. The total sales of the Company were 277,288 tons, a figure slightly less than the previous year, and the total production was 267,900 tons.

The profit for the year, before allowing for depreciation, was Ps. 3,011,053 (£63,550) against Ps. 5,343,019 (£112,700) for the year 1930. A dividend of 5 per cent. was paid for 1930, but the dividend has been passed for the year 1931.

Notes from the Foreign Press.

ABSTRACTED BY J. W. CHRISTELOW, B.Sc.

Hydration of Calcium Aluminate in Portland Cement. K. KOYANAGI. *Zement,* Vol. 20, p. 968, 1931.

It would appear that calcium hydroaluminate has not hitherto been isolated in the pure form from Portland cement clinker; this has now been accomplished and its composition has been established. The author found that under certain conditions clinker gives on hydration large quantities of hydroaluminate crystals. Ground clinker of 30 to 60μ grain size was mixed on an object glass with 1 to 10 parts CO_2-free water, and sealed from the air. A well-burnt clinker of low free CaO content gave thick, short, doubly-refracting needles in 2 to 7 minutes; these later changed into thin hexagonal plates. Staining showed both these forms to be calcium hydroaluminate. In from 20 hours to five days these were converted into doubly-refracting hexagons or pillars, proved to be calcium hydrate. A close connection was found between the free lime content of the clinker and the course of hydration. With a well-burnt clinker of low free CaO content the hydroaluminate crystals soon appeared, with great intensity, while the $Ca(OH)_2$ crystals were very late. With an underburnt clinker (higher free lime) hydroaluminate formation was relatively feeble, and hydroxide appeared earlier.

Large quantities of hydroaluminate were obtained by shaking a ground well-burnt clinker of high Al_2O_3 content with 40 parts water for five minutes (proved to be the optimum conditions), rapidly filtering, and adding an equal volume of lime water to the filtrate. Numerous hexagonal plates were formed after some time, which were rapidly filtered off, washed with alcohol and ether, and dried in a vacuum desiccator; it was important to exclude CO_2 throughout, although contamination could not entirely be avoided. The crystals were analysed, correcting for CO_2 and $Ca(OH)_2$—the latter from the lime water—and found to have the composition $3CaO.Al_2O_3.10.5H_2O$. Their optical properties agreed with those found by earlier workers.

If a smaller volume of lime water was added to this filtrate, the product contained thick short needles more strongly doubly-refracting than the hexagons. The $CaO : Al_2O_3$ ratio of these was 2.7 to 2.8. It would thus appear that on hydration the calcium aluminate of clinker first dissolves as a calcium aluminate of lower lime content than $3CaO.Al_2O_3$, and that this combines with lime, crystallising as tricalcium hydroaluminate.

Water in Concrete. S. GIERTZ-HEDSTRÖM. *Zement*, Vol. 20, pp. 672, 734, 1931.

Two new methods are used in studying the part played by water in concrete. (1) Vapour pressure isothermals are determined by submitting a sample of set cement (broken up to grain size 0.2 to 0.09 mm.) to a stream of air of known humidity at 20 deg. C., obtaining the loss in weight. This is repeated on different samples with air of different humidities. The total water content is obtained by ignition, and the quantity of water retained by the cement (combined water) is found by difference and plotted against the humidity of the air. (2) The free water, defined as the water that can be frozen out of the cement at a certain temperature, is obtained by calorimetric determination of the latent heat of fusion of the ice in frozen samples of set cement of grain size 1.6 to 0.7 mm.

By these means the water in set cement can be separated into three fractions:
(1) firmly combined, *i.e.* water that is not removed even by perfectly dry air;
(2) free, *i.e.* water that can be frozen out of the cement; (3) loosely combined,
i.e. water that can be removed by air but cannot be frozen out. The limits are
not sharply divided.

The quantity of water removed by a stream of air decreases as the humidity
of the air increases. The curve connecting combined water with vapour tension
of water in the air stream is similar to that for silica gel. It has a break at about
6 mm. vapour tension which may separate the adsorbed water from that held
by capillarity. The amounts of both firmly and loosely combined water increase
with the age of the specimen. Aluminous cement always contains more com-
bined water than Portland. The effect of increasing the amount of mixing water
is uncertain; it may increase or diminish the combined water in different cases,
or may hardly affect it. Strength is probably dependent on the combined water,
while shrinkage may depend on the loosely combined water. The percentage
values by weight obtained for a Portland cement are:

Age in days.	Total water.	Firmly combined.	Loosely combined.	Free.
0	26.3	—	—	—
1	27.2	3.5	15.0	8.7
3	27.6	7.0	17.0	3.6
7	29.0	13.0	16.0	0
28	29.8	14.5	15.3	0

The work will be continued.

A New Kiln. H. ENGEL. *Zement*, Vol. 21, p. 291, 1932.

The new kiln described is claimed to be an improvement on the shaft kiln.
It consists of a cylindrical shaft inclined at 45 deg. and slowly rotating on its
axis. Below the cylinder is a cone provided with apertures which come into
contact during rotation with an air-tight clinker discharge; these apertures
are sealed by a conical metal casing when not discharging. Air is blown into
the kiln in three places, axially at the bottom, through the clinker discharge,
and through nozzles disposed around the circumference of the cylinder. The
raw material mixed with fuel is introduced at the top. The raw material can
contain more water than with the normal shaft kiln, and the new kiln is suitable
for use in conjunction with slurry filters. The output per unit capacity is claimed
to be greater than that of the shaft kiln. The principle of the kiln is protected,
and tests with a model have been carried out.

The Ternary Compound $4CaO.Al_2O_3.Fe_2O_3$. S. SOLACOLU, *Zement*, Vol. 21, p. 301, 1932.

Mixtures of the composition of Brownmillerite ($4CaO.Al_2O_3.Fe_2O_3$) were
repeatedly sintered in an electric furnace, and large homogeneous crystals were
obtained whose properties corresponded with those published by Brownmiller.
While these crystals did not contain free lime, a product of composition
$5CaO.Al_2O_3.Fe_2O_3$ contained 10 per cent. free lime. The existence of the compound
Brownmillerite was thus confirmed, and it was shown to be stable in the presence
of free lime. The X-ray spectrum of Brownmillerite did not agree with the
spectra of mixtures of the three binary compounds $2CaO.Fe_2O_3$, $3CaO.Al_2O_3$ and
$5CaO.3Al_2O_3$. It was, however, very similar to the spectrum of $2CaO.Fe_2O_3$,
except that the lines were more widely spaced in the case of Brownmillerite.
Structural analogies with the help of molecular volumes confirmed the iso-
morphism between these two compounds and showed the possibility of mixed
crystal formation.

Recent Patents Relating to Cement.

Portland Cements.

No. 367,505. POLYSIUS AKT.-GES., G., Dessau, Germany. December 30, 1930.

In apparatus for burning or sintering sludgy material *e.g.*, cement, the latter is sprayed or deposited on movable chains (*g*)
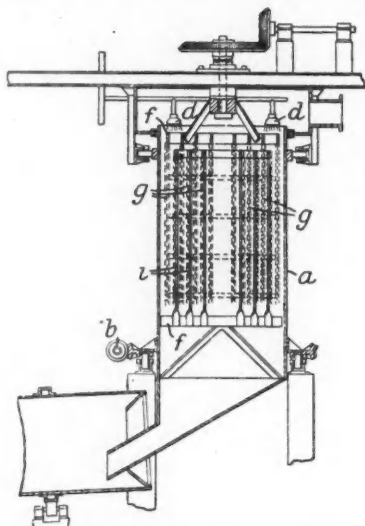
APPARATUS FOR BURNING CEMENT.

or flexible devices traversed by the exhaust gases from a furnace, in which the burning of the material is completed, the material being dislodged from the chains by rotating them on an upper beam (*f*) into contact with stationary members (*i*). The receptacle (*a*) may be rotated by a worm (*b*) and the materials may be sprayed by nozzles (*d*).

PATENTS.

The Proprietors of British Patents No. 275,463 for " Improvements in or relating to the Treatment of Carbonate Materials," and No. 269,480 for " Improvements in or relating to methods of and apparatus for treating materials " desire to introduce their inventions to the notice of manufacturers and others with a view to the inventions being worked commercially under licence or otherwise. All communications to be addressed to Jensen & Son, Chartered Patent Agents, 77, Chancery Lane, London, W.C.2.

Portland Cements.

No. 369,593. ELECTRIC SMELTING & ALUMINIUM Co., 7016, Euclid Avenue, Cleveland, Ohio, U.S.A. (Assignees of Scheidt, A. W., Sewaren, New Jersey, U.S.A.). December 12th, 1930.

The residue of dicalcium silicate obtained by leaching a sinter produced by heating a mixture of aluminous silicious material with an alkali metal carbonate, calcium carbonate, and, if necessary, a material consisting chiefly of alumina (as bauxite) in specified proportions, is mixed with more aluminous material and limestone, and sintered, say in a rotary furnace, for the production of Portland cement.

Grading Analysis and the Properties of Cements.

By D. STEINER.

The following is an abstract of a paper recently published in *Zement*.

Grading Analysis in Cement Grinding.

UNDER given conditions of mill charge, etc., the grading analysis of cement varies only between narrow limits ; this assumes that air separation is not used. Thus a residue of 10 to 12 per cent. on the 180 (per inch) sieve will be accom-

TABLE I.—PERCENTAGE GRADING ANALYSES.

Sieve (meshes per in.) ..	10	20	40	76	180	250
Diameter sieve aperture (in.)	0.06	0.03	0.015	0.008	0.0035	0.0025
Original grit	8.6	39	61	67.5	77.2	81.1
Ground grit I	0.2	2.6	13.8	43.2	61.8	69.2
,, ,, 2			2.6	21.6	45.4	53
,, ,, 3			0.4	8.5	36.6	48
Cement I				4.4	29.7	44.4
,, II				1.7	25.6	39
,, III				1.0	20.8	35
,, IV				0.4	15.4.	28.6
,, V				0.3	9.9	22.2
,, VI				0.2	5.1	14.0
,, VII				0.1	2.1	6.4

panied by 0.5 to 1 per cent. on the 76 sieve if the mill is working properly. A similar relation probably holds for the fraction passing the 250 sieve (particle diameter < 0.0025 in.).
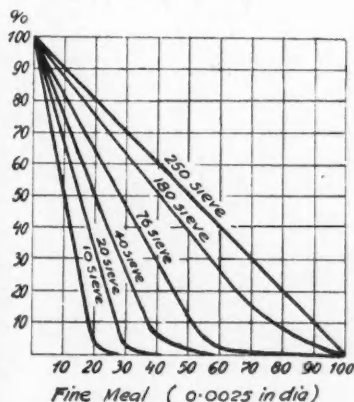
Fig. 1.—Grading of Cements I—VII.
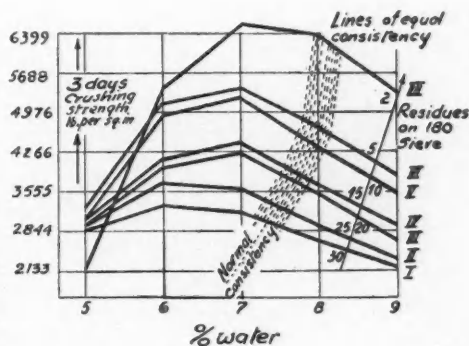
Fig. 2.

Experiments were carried out in which the gypsum-containing clinker grit from the coarse mill was ground in a laboratory mill with cylpebs. Sieve analyses after various periods of continued grinding are given in Table I and Fig. 1. The

first three products are termed " grits " ; the remaining seven products (less than 30 per cent. on the 180 sieve) are named cements I to VII. The fraction passing the 250 sieve is termed " fine meal." In Fig. 1 the grading analysis of each grit and cement is represented by a vertical line, whose position along the horizontal axis is fixed by its percentage of fine meal. The 250-sieve curve is naturally linear. The other curves have a steep linear (proportional) part, followed by a curve which leads to a flattened line. The finer the sieve the less pronounced the curve ; this indicates that the coarser fractions almost entirely
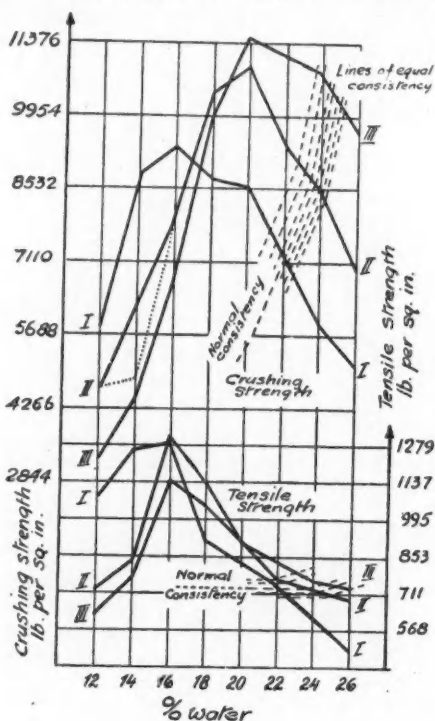
Fig. 3.

disappear in grinding, while the medium-sized grains, cushioned by fine meal, are more difficult to grind. This cushioning effect is greater as the percentage of voids between the grinding media is greater ; cylpebs (10 to 20 per cent. voids) are better than balls (30 to 45 per cent.).

The curves of Fig. 1 are related to mill grading curves. Grinding is most efficient on the proportional part of the curve ; on the other portion, power is being wasted. Most present-day compound mills are thus wasteful of power, as indicated by the 180-sieve curve. A finer sieve than the 180 should, however, be adopted as a criterion of grinding, say the 250-sieve. This is shown by the fact that an air-separated cement is of much inferior quality to a tube-milled cement of the same residue on the 180 sieve.

Fineness, Percentage of Mixing Water and Strength.

Fig. 2 shows the 3-days' crushing-strength curves for 1 : 3 mortars of cements I–VII of Table I, with various percentages of water. Similar tests were made with (I) a cement showing 30 per cent. on the 180 sieve, (II) a commercial cement from the same clinker having 10 per cent. residue, and (III) an unusually fine cement with 2 per cent. residue. The tensile and crushing results of the neat cement are shown in Fig. 3, which indicates the range of equal (normal) consistency. It will be noted that the curves are not parallel. As grinding becomes finer the maximum strength is obtained at higher water contents. It may be concluded that a fall in strength on finer grinding can never be attributed solely to consistency. The crushing strength curves are much more regular than the tensile curves.

The finer cements are susceptible to the influence of too little water, the coarser to excess of water, as is shown by the crushing strengths in Fig. 3. In the region
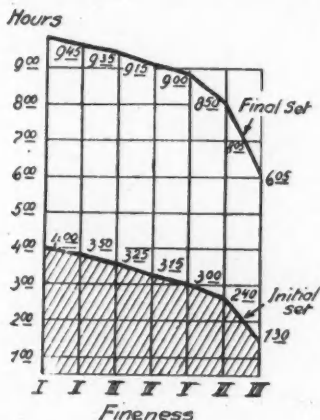
Fig. 4.

of normal consistency the curves are parallel, which is evidence of the correctness of this method of testing.

Relation between Fine Meal and Normal Consistency.

This relation is found to be linear. For a neat cement

Percentage water $= 18.2 + 0.068 \times$ percentage fine meal in cement.

This formula is not valid for quick-setting cements, since with these chemical action sets in during mixing.

Fineness and Setting Time.

At first setting-time is only slightly lowered by increasing the fineness, but as the cement becomes increasingly finer a sudden lowering of setting-time ensues (Fig. 4). It is interesting to note that if standard sand is ground to the fineness of cement, and tested with the Vicat needle in the standard manner, after about four hours the needle will no longer quite penetrate the mass, so that the sand fulfils the definition of initial set. There is, of course, no subsequent hardening.

Effect of Grain Size on Early Strength.

Cements I to VII were mixed with various amounts of stone grit so that each contained the same percentage of fine meal. Strength tests showed equal strengths within narrow limits at three days which proves that the fine meal (diameter < 0.0025 in.) is the principal factor in early strength. It is probable that the diameter of the most important grain size is not much less than 0.0025 in. It must be borne in mind that grinding to zero residue on the 250-sieve would give cement so quick-setting as to be unusable.

Amount of Sand that can be Efficiently Carried by Cement.

Mixtures of 10 to 50 per cent. of a commercial cement with sand were tested. The curve of seven days' crushing strength increased slightly up to 15 per cent. cement, and then rapidly up to 35 per cent., after which the increase of strength again became slow, asymptotically approaching the strength of the neat cement. The rapidly rising portion of the curve represents the most economical mixes.

Trade Notice.

Excavators.—In their latest excavator list Messrs. Ruston-Bucyrus, Ltd., of Lincoln, give a number of interesting photographs taken in their works showing some of the various stages in the production of their machines. The list also illustrates many of the various types of excavators, and gives full specifications, sizes, weights, and notes on the equipment of each type.

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